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OPERATIONS HANDBOOK FOR THE AEROCHEM PROTOTYPE CONTINUOUS CHEMILUMINESCENCE NO MONITOR

Final Report

Richard J. Ronco and Arthur Fontijn

May 1971

Prepared for

AIR POLLUTION CONTROL OFFICE

ENVIRONMENTAL PROTECTION AGENCY

Research Triangle Park, N.C. 27709

Contract CPA 70-79

AeroChem Research Laboratories, Inc.

SYBRON CORPORATION

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A prototype ambient air NO monitor (based on the NO/O3 chemiluminescent reaction) which was designed, fabricated, and delivered is discussed in detail. Design considerations are also discussed.

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FOREWORD AND ACKNOWLEDGMENT

Under our contract CPA 22-69-11 (August 1968-September 1969), the feasibility of using the NO/O_3 chemiluminescent reaction for selective quantitative monitoring of NO had been demonstrated. Under the present contract CPA 70-79 (May 1970-May 1971) a prototype ambient air NO monitor based on the NO/O_3 reaction has been designed, fabricated, and delivered to the APCO Project Officer. The present report gives a detailed discussion of this prototype instrument as well as design considerations.

We are indebted to R.K. Stevens, APCO Project Officer on both contracts, as well as to J.A. Hodgeson and A.E. O'Keeffe of APCO for useful advice. The measuring electronics package has been designed with the aid of W.W. Brenner and H.S. Reichard, AeroChem Electronics Consultants. We have also benefited from discussions with A.J. Sabadell, H.F. Calcote, and F.H. Raab of AeroChem and with several technical representatives of manufacturers, whose equipment is incorporated in the monitor. M.D. Shaltis has capably assisted in the assembly of the instrument.

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I. SPECIFICATIONS

PRINCIPLE OF MEASUREMENT	Gas phase chemiluminescence.
TYPE OF MONITORING	Continuous.
USEFUL CONCENTRATION RANGE	≈ 2 ppb* to ≈ 200 ppm NO in air.
ATMOSPHERIC INTERFERENCES	None.
MEASURING RANGES	Five decade ranges: 0-10 ppb 0-100 ppb 0- 1 ppm 0- 10 ppm 0-100 ppm.
SPAN	Continuously adjustable multiplication of any decade range by factors from 1 to 10.
ACCURACY	Determined by the accuracy of the calibration gas sample (typically ± 5%).
ELECTRONICS	All solid state.
READ OUT	Large scale analog panel meter.
RECORDER OUTPUT	0-1 VDC.
CALIBRATION	Automatic every 8 hours; manual as desired.
TIME LAG†	50 seconds (for normal inlet). 5 seconds (for auxiliary sample inlet).
RISE TIME§	10 seconds.

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* Defined as the minimum signal detectable above background noise.

† Defined as the lapse in time between the introduction of a sample and the initial meter response.

§ Defined as the period of time, following the time lag, required for a signal to reach 90% of its ultimate value.

POWER REQUIREMENTS	115 VAC (1% regulated) 60 Hz, 400 W (exclusive of vacuum pump).
VACUUM PUMP	Explosion proof, 3.5 CFM mechanical, 115 VAC, 60 Hz, 700 W.
DIMENSIONS	18"h × 22"w × 20"d.
WEIGHT	110 lbs.
EXTERNAL CONNECTIONS	Vacuum pump. Oxygen and calibration gas cylinders. Line voltage regulator.

II. GENERAL DESCRIPTION

A. Principle of Measurement*

A schematic design of the chemiluminescence detector is shown in Fig. 1. The air (analyte) being monitored and the second reactant, partially ozonated oxygen (≈ 0.5% v/v), enter the reaction vessel (p ≈ 1 Torr) through separate inlets. Rapid mixing occurs and a chemiluminescent reaction takes place:

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad (1)$$

$$NO_2^* \rightarrow NO_2 + h\nu \quad (2)$$

The intensity of the light emitted is measured by the photomultiplier tube and associated read-out devices (current meter and recorder). After calibration with samples of known concentration, a continuous record of the concentration of the pollutant in air is obtained.

The light intensity, I, of the NO/O_3 reaction is given by:[3]

$$I = k[NO][O_3]/P \quad (3)$$

in which

k = rate coefficient (proportionality constant)
[ ] = denotes concentrations
P = Pressure

Thus at a constant pressure and O_3 concentration, the intensity, and hence the phototube current reading, is linearly proportional to the amount of NO flowing through the system.

The spectral distribution of the NO/O_3 chemiluminescent emission is shown in Fig. 2. The phototube being used is responsive to radiation over the 0.35 to 0.85 μ range. Since as Fig. 2 shows the NO/O_3 radiation is emitted at wavelengths larger than 0.6 μ a light filter passing only such radiation is placed in the light path (see Fig. 1), thus minimizing the chances for accidental measurements of interfering emissions by other reactions.

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* For a more detailed description see the reports on the feasibility study, Refs. 1 and 2.

B. Instrument Functions

The basic functions are shown schematically in Fig. 3.* They may be subdivided into the gas flow system, the light detection system and the calibration functions.

The principal gas handling system consists of an ambient air (sample) flow line and an ozonated oxygen flow line. The volume flow rate is controlled at a preset value by the sonic orifices. The gases mix in the reactor and the flow is maintained by the mechanical vacuum pump. For use of the instrument as a research tool, an auxiliary sampling system has been provided, through which the flow can be controlled manually with a needle valve (under normal conditions this line is closed by means of a toggle valve).

The light detection system consists of the thermo-electrically cooled photomultiplier tube, the phototube high voltage power supply, and the measuring electronics package to which are connected the current meter (calibrated in terms of NO concentration) and the recorder output.

To calibrate the instrument the ambient air inlet can be closed by the 3-way solenoid valve, A, and be replaced by a flow containing a known amount of NO (calibration gas). To rezero the electronics the sample flow side is closed off entirely by the solenoid valve B. Both these calibration functions are carried out automatically at fixed intervals controlled by the time programmer; they can also be initiated by the operator by means of pushbuttons located on the front panel.

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* A detailed description is given in Section III.

III. DETAILED DESCRIPTION

Figures 4 and 5 show the front and rear panels of the monitor. Figures 6, 7 and 8 are photographs of the inside of the instrument showing the location of the major components, to be discussed below.

A. Gas Handling System

1. Reactor

The one liter spherical reactor has been fabricated from 16 gauge type 316 stainless steel; it has a reactant nozzle inlet flange on the top, a vacuum outlet tube on the bottom, and an optical window on the side. A thermocouple vacuum gauge (Hastings Raydist VT-4/DV4R), consisting of a noble metal thermocouple and a corrosion-resistant housing, is attached to the vacuum outlet tube (1-1/8 inch o.d. type 316 stainless steel). The 2 inch o.d. quartz optical window is held in place by an ethylene propylene O-ring flange.*

2. Gas Feed Lines

The gas feed line functions can best be followed from Fig. 3. The tubing used is 0.25 inch o.d. (0.016 inch wall) type 316 stainless steel.

a. Primary Reactant (Analyte) - Ambient air is drawn into the system through a coarse filter (Hoke No. 6325G4Y) and then through the three-way stainless steel solenoid valve A (Asco No. 832069 VH). The valve normally passes ambient air, but is automatically switched every 8 hours to allow the calibration gas to flow during the calibration cycle. The air† passes through a 5 micron sintered stainless steel filter (Hoke No. 6321G4Y) and

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* These O-rings are specifically resistant to ozone. Bulletin 5721, Parker Seal Co. (Culver City, Calif.) 1970.

† The presence of H_2O vapor in the reactor does not interfere with the NO measurement.[1,2] However, it is conceivable that during very warm and humid periods H_2O might condense in the flow lines and interfere with the NO flow. If problems are encountered during such periods the dryer provided with the instrument (stored on the bottom plate, see Fig. 6) should be filled with indicating activated alumina and be installed in the space provided in the flow line just upstream of the 5 micron filter.

then through the sonic flow orifice* (Richard Bird Co., Model RB-282J). The flow through this orifice is 0.8 cc (STP) sec^{-1}. The orifice is located on the downstream side of the filter holder (Hoke No. 632164Y) for maximum protection against clogging. The air then passes through the stainless steel solenoid valve B (Asco No. 8262C3SVH) which is automatically closed during the periodic background current suppression cycle. Finally, the air enters the reactor through the Pyrex nozzle.

A common flow path is provided for the air and calibration gas wherever possible. The calibration gas is best delivered to the instrument at a pressure of about 2 psi by a two-stage corrosion resistant regulator. A low-pressure regulator (Conoflow Corp. H10XT1014K) located inside the instrument (Fig. 3) reduces this pressure to atmospheric, to provide the same flow condition for the calibration gas as for the analyte air.

An auxiliary gas inlet line has been added to the primary reactant line. The use of this input will allow the introduction of a gas flow directly into the reactor without going through the sonic orifice-filter system. The gas flow is controlled with a needle valve and a toggle valve located inside the instrument. These valves are accessible through the removable panel on the right hand side of the instrument.

b. O_3/O_2 Feed Line - Cylinder O_2 passes through a stainless steel dryer filled with indicating type activated alumina; a Plexiglas flange cover is provided to allow visible observation of the condition of this drying agent. The O_3 is produced at a concentration of $\approx 0.5\%$ v/v by passage of the O_2 through the photolytic ozonator (OREC 03V1-O/5). The remaining components such as the low-pressure regulator, micron filter, and sonic orifice, are duplicates of the components used in the primary reactant flow line. The O_3/O_2 enters the reactor through a Pyrex nozzle.

B. Light Detection System

The photomultiplier tube housing (Products for Research TE-102 TS) is flange mounted directly to the reactor, to allow the photocathode to be situated as close as possible to the reactor and obtain a light-tight assembly. The housing is thermo-electrically/air cooled to -15°C and regulated to within ± 0.5°C by an external power supply. The radiation entering the housing passes through a specially designed thermopane window which provides a thermal break between the reactor and the phototube and prevents window fogging. The

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* We have considered thermostating the flow orifices. However, normal room temperature variations of ± 5°C would produce only a ± 1% change in gas flow rate (and a comparable change in signal), which appears too minor to require correction.

thermopane window consists of a Corning CS 2-60 light filter disc and a clear Pyrex disc separated by a Plexiglas cylinder and is filled with dry nitrogen. The filter cuts off radiation of $\lambda < 6100$ Å. The housing also provides electrostatic and electromagnetic shielding for the phototube.

The radiation is monitored with an EMI 9558A trialkali photomultiplier tube, operated at 1950 VDC. The spectral response curve is shown in Fig. 9. The power supplies used in the light detection system are discussed in the Electronics Section (III.D.).

C. Calibration Functions

1. Automatic Calibration

In order to rezero and calibrate the instrument the time programmer master control (Automatic Timing and Controls 324COIL2CRIAOIX) engages an automatic sequence every 8 hours. This 5 minute sequence is controlled by the time programmer sequence control (Automatic Timing and Controls 324CO7E3ERIAOIX) and is shown schematically in Fig. 10. This 5 minute sequence consists of four steps: steps a and b form the rezero cycle and steps c and d the nitric oxide signal cycle.

Step a - The solenoid valve, B (Fig. 3), closes the primary reactant line. At the end of the rezero cycle it returns the instrument to the normal operating condition.

Step b - The electronic autobalance cycle is engaged and automatically adjusts the background* signal to zero by applying a current of reverse polarity.† The balance cycle is held in the engaged position for 30 seconds, to time average the background signal. During this balance cycle the most sensitive range (0-10 ppb) is automatically selected regardless of the (front panel) range switch setting. When the cycle is complete the range will automatically return to the setting indicated by the range switch.

Step c - The 0-1 ppm range is automatically selected regardless of the range switch setting. When the cycle is complete the range will automatically return to the setting indicated by the range switch.

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* That signal produced by the unidentified radiation resulting from passage of ozonated oxygen through the reactor.

† Such balance currents are also commonly referred to as "current offset", "current suppression" and "buck out".

Step d - The solenoid valve, A, is energized and the calibration gas* is allowed to flow through the reactor, thus yielding the calibration point on the meter and recorder.

2. Manual Initiation Options

a. The full automatic calibration cycle can be initiated at any time by depressing the AUTO CALIB button on the front panel. Once engaged the cycle will run in exactly the same manner as described under automatic calibration (Section III.C.1). This procedure does not influence the automatic 8-hour initation.

b. The electronic autobalance cycle, can be engaged by first closing valve B and then pushing the BALANCE button on the front panel.

3. Manual Calibration Sample Introduction

Calibration flows can also be manually introduced into the system at any time. We have found the following procedure to be very convenient: Fill a ≈ 25 cc graduated syringe with a known concentration of calibration gas (e.g. from the calibration cylinder), remove the needle and connect the syringe to the sample inlet with a short piece of flexible tubing. The calibration sample will then be drawn into the monitor at a rate which can be directly measured by observing the rate of movement of the plunger. The concentration of calibration gas remains constant until the syringe is empty.

D. Electronics

1. Measuring Electronics Package

The basic functions of the measuring electronics package are to amplify the photomultiplier tube current with an electrometer type amplifier and to reduce the noise component of the signal. A 6-inch panel meter (analog type) is mounted on the front panel and monitors the measuring electronics

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* The gas recommended for calibration is N_2 containing ≈ 0.5 ppm of NO. In our work this gas contained 0.39 ± 0.02 ppm NO, according to the supplier's (Scott Research Laboratories, Plumsteadville, Pa.) analysis.

output. This meter is calibrated in parts per billion of nitric oxide. A 0-1 VDC recorder output connection is provided on the rear panel. The measuring electronics package also contains a phototube overload protection circuit, a zero suppression circuit to balance the instrument noise and the automatic range selection for the calibration cycle. A block diagram is given in Fig. 11, and complete schematics are shown in Figs. 12A-12E.

a. Current Input and Ranging - The measuring electronics package, Fig. 11, is connected to the photomultiplier tube socket at the ANODE connection with a coax cable (RG58/U). This current is amplified, filtered and read out on the front panel meter. Five current ranges can be manually selected with the decade RANGE switch on the front panel: 0-10 ppb, 0-100 ppb, 0-1 ppm, 0-10 ppm, 0-100 ppm. The SPAN ADJUST control (normally set to 1.00 on the dial) is continuously adjustable and can be used to set any full scale range within the operating limits of the instrument.
NOTE: Do not use SPAN ADJUST settings below 1.00 since the current measuring electronics is non-linear at such settings.

b. Phototube Protection Circuit - The phototube would be damaged if the maximum allowable anode current (1mA) were exceeded. Therefore a protection device (located in the measuring electronics package), which removes the high voltage from the photomultiplier tube is built in. This device, Fig. 11, consists of a current sensing circuit and a high voltage relay, which can also be tripped by the front panel PMT OFF button.
CAUTION: The phototube protection device and the PMT OFF button do not turn off the high voltage power supply and dangerous voltage thus remains inside the instrument.

c. Balance Circuit - A noise current suppression device, Fig. 11, has been built into the measuring electronics package to suppress the background signal to near zero. This noise current suppression will hereafter be referred to as balance. Since the background signal is not a pure DC or a steady signal but rather a random low frequency composite, the background can best be considered as a band of noise. This band of noise when observed on the most sensitive instrument range (0-10 ppb NO) has, after balancing, a maximum value of about 20% of full scale. This band of noise represents the limiting factor in the maximum instrument sensitivity. The balance circuit consists of a current sensing device, range control relays and a motor-driven potentiometer. The circuit is manually engaged by the BALANCE button on the front panel or automatically by the time programmer. When operating, the most sensitive range is automatically selected regardless of range setting. The average noise is suppressed to zero by the motor driven potentiometer (Beckman Instruments Model No. 939R50KL.2G560). Upon completion of the balancing operation the range is returned to the setting indicated on the range switch.

The balance circuit also contains an offset current interrupt switch which is operated by keeping the ANODE CURRENT pushbutton on the front panel depressed. In this way, the phototube anode current is observed directly on the front panel meter (read "nA" for "ppb"), which gives a measure of the amount of offset current being used. Knowledge of the phototube current is helpful in troubleshooting.

2. Phototube Power Supply

The phototube high voltage power supply (Computer Power Systems 2500 N/1254) is mounted inside the instrument on the rear panel (Fig. 8). The output voltage is preset at 1950 VDC.* This high voltage is supplied to the phototube by a coax cable (RG59/U) through the high voltage relay.
CAUTION: High voltages exist at the power supply output connector, cable, and high voltage relay.

3. Cooled Housing Power Supply

This power supply, Fig. 8, provides the 6 VDC power for the thermoelectric heat pump of the phototube housing and the line voltage for the fan motor used to circulate air over the thermoelectric heat exchanger. This supply remains on as long as power is supplied to the monitor.

4. Ozonator Power Supply

This power supply is contained in the ozonator housing (see Section III. A. 2).
CAUTION: The ozone lamp is powered by a 5000 VAC high voltage transformer. A safety device (cover interlock switch) turns off the line voltage if the ozonator cover is removed. Care should be taken not to come in contact with the transformer.

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* For the intended operation of the monitor this voltage should not be changed. However, it may be useful to mention that a 5% adjustment screw is located on this power supply (see Fig. 8) and that installation of other internal programming resistors allows the selection of other voltages in the range -500 to -2000 Volts (for details see the Computer Power Systems instruction manual supplied with the instrument).

IV. OPERATING INSTRUCTIONS

A. Description of Panels and Controls

1. Front Panel (see Fig. 4)

METER	The meter continually displays the concentration of nitric oxide being measured by the instrument. The scale is calibrated from 0-10 parts per billion.
METER RESET	Zeros the meter when held depressed.
RANGE SWITCH	Selects the instrument measuring range from any one of five full scale ranges: $\times 1$, $\times 10$, $\times 10^2$ $\times 10^3$, $\times 10^4$, corresponding to 10, 10^2, 10^3, 10^4 and 10^5 ppb full scale.
SPAN ADJUST	Used to set any full scale range between the decade range switch settings.
POWER ON	Connects and disconnects the line voltage to the electronics measuring package and the phototube power supply. Power is on when pushbutton is lighted.
PMT ON	Turns on the high voltage to the phototube by operating the high voltage relay. Phototube power is on when pushbutton is lighted.
PMT OFF	Turns off the high voltage to the phototube by tripping the high voltage relay. Phototube power is off when this button is lighted.
BALANCE	Engages the balance circuit, zeroing the instrument. When this button is lighted the instrument is balancing.
AUTO CALIB	Engages the time programmer and calibrates the instrument. When this button is lighted the instrument is calibrating.
ANODE CURRENT	When held depressed shows the phototube anode current on the meter; under these conditions read "nanoamps" in place of "ppb". This button does not light up.

VACUUM GAUGE	Shows the reactor pressure.

2. Rear Panel (see Fig. 5)

RECORDER OUTPUT	0-1 VDC. Follows the front panel meter.
RECORDER ADJUST	Used to match the recorder to the meter.
AIR INLET	In normal operation the sample air is drawn into the instrument through this connector.
CALIBRATION INLET	The calibration gas flows into the instrument through this connector.
OXYGEN INLET	The O_2 to be ozonated flows in through this connector.
AUXILIARY AIR INLET	Air can be drawn into the instrument through this connector.
VACUUM	Connector to the vacuum pump.
CONTROL SWITCH FOR SOLENOID VALVE B	In normal operation this switch should be in the "open" position. When closed analyte NO will not flow into the reactor.

B. Installation

Step a - Place the instrument on a suitable support such as a table or bench, so that air can circulate through the monitor. Cooling air is taken in through louvers in the bottom of the monitor, and is exhausted through the louvered side. For good air circulation allow at least 6 inches of free air space on the left (louvered) side of the monitor.

Step b - Connect the vacuum pump to the monitor using the connectors and tubing provided. A three-foot long stainless steel tube is supplied with the instrument and can be cut to any desired length.
NOTE: The 3.5 CFM vacuum pump (Edwards ES 100) supplied with the instrument is filled with Dow Corning Fluorosilicone (FS 1265 30CS) fluid. Regular hydrocarbon base oils should not be used since they deteriorate when pumping ozonated oxygen and may explode.

Step c - Connect a good commercial grade oxygen cylinder via a pressure regulator to the OXYGEN INLET connector on the rear panel. The inlet pressure should be about 2 psi. A standard size (≈ 240 cu. ft.) cylinder is

recommended for operational convenience.
NOTE: Purge the gas line well before connecting to the monitor.
CAUTION: Inlet pressures above 5 psi can damage the pressure regulator inside the monitor.

Step d - Connect the air supply to be monitored to the AIR INPUT connector on the rear panel.
NOTE: To minimize response time the connection between the air inlet and air source should be kept as short as possible and be made of narrow tubing (e.g. 0.1 inch i.d.).

Step e - Connect a supply of calibration gas at a pressure of about 2 psi to the CALIBRATION INLET connector on the rear panel. For ambient air monitoring calibration gas having a concentration of no more than about 0.5 ppm NO in N_2 is recommended.
CAUTION: Inlet pressures above 5 psi can damage the pressure regulator inside the monitor.

C. Operation

Step a - Turn the solenoid valve "B" control switch (rear panel) to the "closed" position.

Step b - Turn the RANGE switch to the $\times 10^4$ position.

Step c - Set the SPAN control to 1.00 (1 in window, 0 on dial).

Step d - Turn on the vacuum pump by connecting it to a standard 115 Volt AC electrical outlet.

Step e - Connect the instrument power cord (rear panel) to a regulated 115 Volt AC outlet using the regulator provided.
NOTE: To minimize electronic noise this regulator should be positioned several feet away from the instrument.
CAUTION: The instrument should be connected to an electrical ground using the three-prong plug provided.

Step f - Depress the POWER ON button on the front panel. The button will light up.

Step g - Allow at least two hours for the phototube to automically cool to -15°C. During this period the phototube dark current will decrease by about two orders of magnitude. In the following seven days the phototube dark current will gradually decrease by about one more order of magnitude. Hence in the first week the instrument will not be at full sensitivity.

Step h - Hold the METER RESET button depressed and adjust the reading to zero using the mechanical meter zero screw.

Step i - Depress the PMT ON button which will light up.

Step j - Move the range switch to a lower scale so that a meter reading is obtained.

Step k - Depress the BALANCE button which will light up. The light will go off when the zeroing operation is complete. Repeat if necessary.
NOTE: During automatic calibration this button may light up intermittently as the instrument repeats the zeroing operation.

Step l - Turn the solenoid valve B control switch (rear panel) to the "open" position.

Step m - The instrument is now measuring the level of nitric oxide flowing in from the ambient. To read-off the NO concentration set the RANGE switch and SPAN ADJUST to the ranges desired.

Step n - The instrument will automatically rezero and give a calibration signal every 8 hours (cf. Section III.C.1). If calibration is desired at any other time push the AUTO CALIB button; the instrument then will rezero itself and give a calibration point. If the calibration point does not register at the correct reading, adjust the calibration potentiometer as described in Section IV.D.2.
NOTE: The AUTO CALIB botton has to be held depressed for about 7 sec before it engages. Engagement is indicated by the light remaining on after the button has been released.

D. Maintenance

1. Planned Maintenance

O_2 DRYER - The indicating type, activated alumina drying agent (viewed through the window on the dryer top) should be changed as needed. The average life of one charge corresponds to at least three months continuous operation.

AIR DRYER - If the air dryer (Section III.A.2) is in use the activated alumina (indicating type) drying agent should be refilled as needed. The dryer has a large enough capacity to last for at least 3 weeks when the relative humidity is 100% at 35°C.

O_2 CYLINDER- Change the oxygen cylinder before the cylinder is completely empty to avoid possible damage to the ozonator under vacuum conditions. A standard size cylinder will last for about nine weeks, based on continuous flow rate of 0.8 cc (STP) sec^{-1} and a cylinder capacity of ≈ 240 cu.ft.
NOTE: Purge the oxygen line well after connecting a new cylinder.

VACUUM PUMP- Check the oil level and drive-belt wear occasionally.
NOTE: The vacuum pump is filled with fluorosilicone oil. Dot not use hydrocarbon oils, cf. Section IV. B.
CAUTION: Toxic vapors may be produced from this oil by heating; use with adequate ventilation.

GAS FLOWS - Check the vacuum gauge occasionally. The gauge pressure should be about 1.0 Torr. A change in gas flow conditions, such as a partially obstructed flow line, will show up on the vacuum gauge.

ANODE CURRENT - Check the phototube ANODE CURRENT occasionally with the solenoid valve B closed. Under these conditions this current should not exceed 400 nA as this exceeds the balance circuit capability and is indicative of a malfunction (see Section IV. E).

FILTERS - Change the coarse and fine filters (Fig. 3) as needed, depending on local ambient conditions. The filters can best be cleaned in an ultrasonic clearer.

2. Signal Calibration

An internal calibration potentiometer is provided in the electronics measuring package (board 3 marked CALIBRATION POT (Fig. 7)). This potentiometer is preset to match the current indicated on the panel meter against a known concentration of nitric oxide. The potentiometer setting should not be changed unless the calibration point on the meter does not agree with the known calibration gas concentration. In that case perform the following steps:

Step a- Turn the solenoid valve "B" control switch (rear panel) to the CLOSED position.

Step b - Wait one minute; depress the BALANCE button which will light up. The light will go off when the balance cycle is complete. Repeat if necessary.

Step c - Move the RANGE switch and the SPAN ADJUST to obtain a range of 0-1 ppm.

Step d - Flow in the calibration gas (≈ 0.5 ppm NO in N_2). Adjust the potentiometer until the reading on the meter scale matches the known concentration of NO in the calibration gas.

E. Troubleshooting

Procedures to guide troubleshooting are given on the following chart:

TROUBLESHOOTING CHART

Symptom	Possible Cause	Correction
1. Panel meter at zero, no needle movement.	a) Blown fuse (rear panel).	Replace fuse.
	b) Blown fuse in PMT high voltage power supply	Replace fuse.
2. Anode current increase, in excess of 1 μA.	a) PMT housing power supply output too low.	Check fuse, check the high voltage output, repair if necessary.
	b) Light leak in the light detection system	Tighten the O-ring between the PMT housing and the reactor.
	c) Normal air circulation through the monitor has been restricted.	Allow adequate air flow. See installation instructions.
3. PMT high voltage off as indicated by a total loss of signal and by the front panel pushbuttons.	a) A concentration of nitric oxide in excess of 1000 ppm has been introduced into the monitor, tripping the photo tube overload device.	Wait fifteen (15) minutes, reset by depressing the PMT ON button.
	b) A light leak has developed in the light detection system.	Tighten the O-ring between the PMT housing and the reactor.
4. Reactor pressure is one half of the normal pressure (≈ 0.5 Torr).	a) The BALANCE-MEASURE switch is in the BALANCE position.	Return the switch to the MEASURE position.
	b) The oxygen gas cylinder is empty.	Replace the oxygen cylinder.
	c) A sonic flow orifice is clogged restricting the normal flow.	Remove the orifice/filter holder and clean in an ultrasonic cleaner.
5. Balance cycle engages (as indicated by the lighted BALANCE button) but will not disengage.	a) The balance cycle was engaged while the monitor was measuring an NO concentration in excess of 1 ppm.	Step 1 - Depress the PMT OFF button and then depress the PMT ON button. Step 2 - Move the solenoid valve B control switch to the CLOSED position. Wait one minute. Balance. Return the switch to the OPEN position.
	b) The balance current offsetting limit has been exceeded by a light leak raising the anode current above 1 μA.	Follow Steps 1 and 2.
6. The reactor pressure is higher than ≈ 3.0 Torr.	A leak in the gas handling system has developed.	Move the BALANCE-MEASURE switch to the BALANCE position. Isolate the leak by standard leak detection methods and repair.

V. DESIGN CONSIDERATIONS AND TESTS

A. Stainless Steel Gas Flow System

A spherical Pyrex reactor had been used in the feasibility study.[1,2] However, a metal reactor appeared more suitable for a rugged compact design for the prototype instrument and moreover is easier to assemble and disassemble.

To evaluate this idea a 1 liter type 316 stainless steel reactor was substituted for the Pyrex reactor in the apparatus used in the feasibility study. This substitution yielded a slightly lower background noise (measured by flowing only ozonated oxygen through the apparatus) and did not affect the NO/O_3 signal strength. The limit of sensitivity thus is slightly improved using the stainless steel reactor, which was subsequently incorporated in the prototype instrument.

Other parts, such as the phototube housing, were also first tested on the feasibility study apparatus, before deciding whether to incorporate them into the prototype monitor.

B. Photomultiplier Tube Selection

On the basis of the available manufacturers' literature and in consultation with several phototube manufacturers, a number of tubes were borrowed for a series of tests. These tests were performed on the research apparatus[1,2] under identical system conditions, using a Keithley 602 electrometer and maximum background current suppression. The results of this comparison are given in the following table:

PHOTOMULTIPLIER TUBE COMPARISON AT -20°C*

PMT	Applied Voltage, V	Dark Current, A	Total Background Current, A	Maximum Sensitivity, ppb NO	Cost, $
EMI 9558QA	1400	3×10^{-9}	3×10^{-8}	4	700
EMI 9659A	2000	4×10^{-10}	4×10^{-9}	3	900
EMI 9658A	2000	2×10^{-7}	1×10^{-6}	15-20	700
RCA C31000E	2800	3×10^{-8}	4×10^{-7}	15-20	750
RCA 7164R Selected	2000	1×10^{-10}	1×10^{-9}	75	200

*Differences between individual tubes occur in any given tube type. However, the manufacturers loaned us the best available tubes for this comparison, which therefore has qualitative validity.

On the basis of these tests both the EMI 9558 QA and 9659 A tubes appeared suitable for incorporation into the prototype. However, the 9659 A also had to be rejected since the signal received from this tube at NO concentrations below about 30 ppb cannot be detected with the prototype electronics (lowest current range is 10 nA full scale; higher sensitivity would have added considerably to the instrument cost).

Tests on the prototype monitor showed the 9558 QA noise level at 1400V (where the S/N is most suitable for detection of weak signals) to be an order of magnitude less than the noise in the chemiluminescence signal. As a result we found phototube gain to be the controlling factor in achieving the lowest limit of sensitivity and the best results were obtained with 9558 family tubes operated near their maximum allowable voltage (2000 V). A number of 9558 QA and A tubes* then were compared and the one with the highest gain was incorporated in the prototype.

C. Measurement of the Background Signal

The technique used in the prototype for measuring the background signal is to close solenoid valve B, i.e. to allow only the ozonated oxygen (secondary reactant) to flow through the reactor.† Since this measurement is thus made at half the total flow rate and pressure used when measuring NO, a test of the validity of this procedure was required.

The test used was to flow O_2 in through the auxiliary gas inlet line. Under this condition no NO flows into the reactor, but the total flow and pressure are the same as when valve B is opened and air is being sampled. No difference in signal could be observed between this condition and the primary reactant side closed-off condition, obtained during this test by closing the toggle valve in the auxiliary inlet line.

It must be concluded that the instrument reading obtained in normal operation when valve B is closed gives the true background signal.

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* Apart from the extended ultraviolet response of the QA (quartz envelope), which is of no use in the present application, the 9558 QA and A tubes are identical.

† Under these conditions the signal measured is a combination of phototube dark current and unidentified light emission due to the O_2/O_3 flow.

D. Linearity of Response

The linearity of response was tested in the same manner as during the feasibility study,[1,2] i.e. by injecting known samples of NO into an exponential dilution flask (connected to the auxiliary air inlet).* No deviation from linearity over the 2 ppb to 200 ppm range could be observed. Above 200 ppm deviations from linearity begin to occur.

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* The meter readings obtained from given samples were found to be the same whether they were introduced through the auxiliary or the normal air inlet as long as the same flow rate was maintained. For this inlet system comparison the samples were introduced as described in Section III.C.3.

VI. REFERENCES

1. Fontijn, A., Sabadell, A.J. and Ronco, R.J., "Homogeneous Chemiluminescent Measurement of Nitric Oxide with Ozone. Implications for Continuous Selective Monitoring of Gaseous Air Pollutants," Anal. Chem. 42, 575 (1970).

2. Fontijn, A., Sabadell, A.J. and Ronco, R.J., "Feasibility Study for the Development of a Multifunctional Emission Detector for Air Pollutants Based on Homogeneous Chemiluminescent Gas Phase Reactions," Aero-Chem TP-217, Final Report, Contract CPA 22-69-11, September 1969.

3. Clyne, M.A.A., Thrush, B.A. and Wayne, R.P., "Kinetics of the Chemiluminescent Reaction between Nitric Oxide and Ozone," Trans. Faraday Soc. 60, 359 (1964).

4. Clough, P.N. and Thrush, B.A., "Mechanism of Chemiluminescent Reaction between Nitric Oxide and Ozone," Trans. Faraday Soc. 63, 915 (1967).

VII. LIST OF MANUFACTURERS

Manufacturer or Vendor	Item
Amersil, Inc. Hillside, N.J. 07205	REACTOR WINDOW
API Instruments Co. Chesterland, Ohio 44026	PANEL METER
Automatic Switch Co. (ASCO) Florham Park, N.J.	SOLENOID VALVES
Automatic Timing & Controls, Inc. King of Prussia, Pa. 19408	TIME PROGRAMMER
Beckman Instruments Fullerton, Calif. 92634	MOTOR POTENTIOMETER
Computer Power Systems, Inc. Sunnyvale, Calif. 94086	PHOTOTUBE POWER SUPPLY
Conoflow Corp. Blackwood, N.J. 08012	LOW PRESSURE REGULATORS
Edwards High Vacuum, Inc. Grand Island, N.Y. 14072	VACUUM PUMP
Gencom Division Varian/EMI Plainview, N.Y. 11803	PHOTOTUBE
Hastings-Raydist Co. Hampton, Va. 23361	VACUUM GAUGE
Ozone Research & Equipment Corporation (OREC) Phoenix, Ariz. 85019	OZONATOR
Parker Seal Co. Culver City, Calif. 90230	O-RINGS
Products for Research, Inc. Danvers, Mass. 01923	PHOTOTUBE HOUSING
R.H. Bird Co. Waltham, Mass. 02154	SONIC ORIFICE

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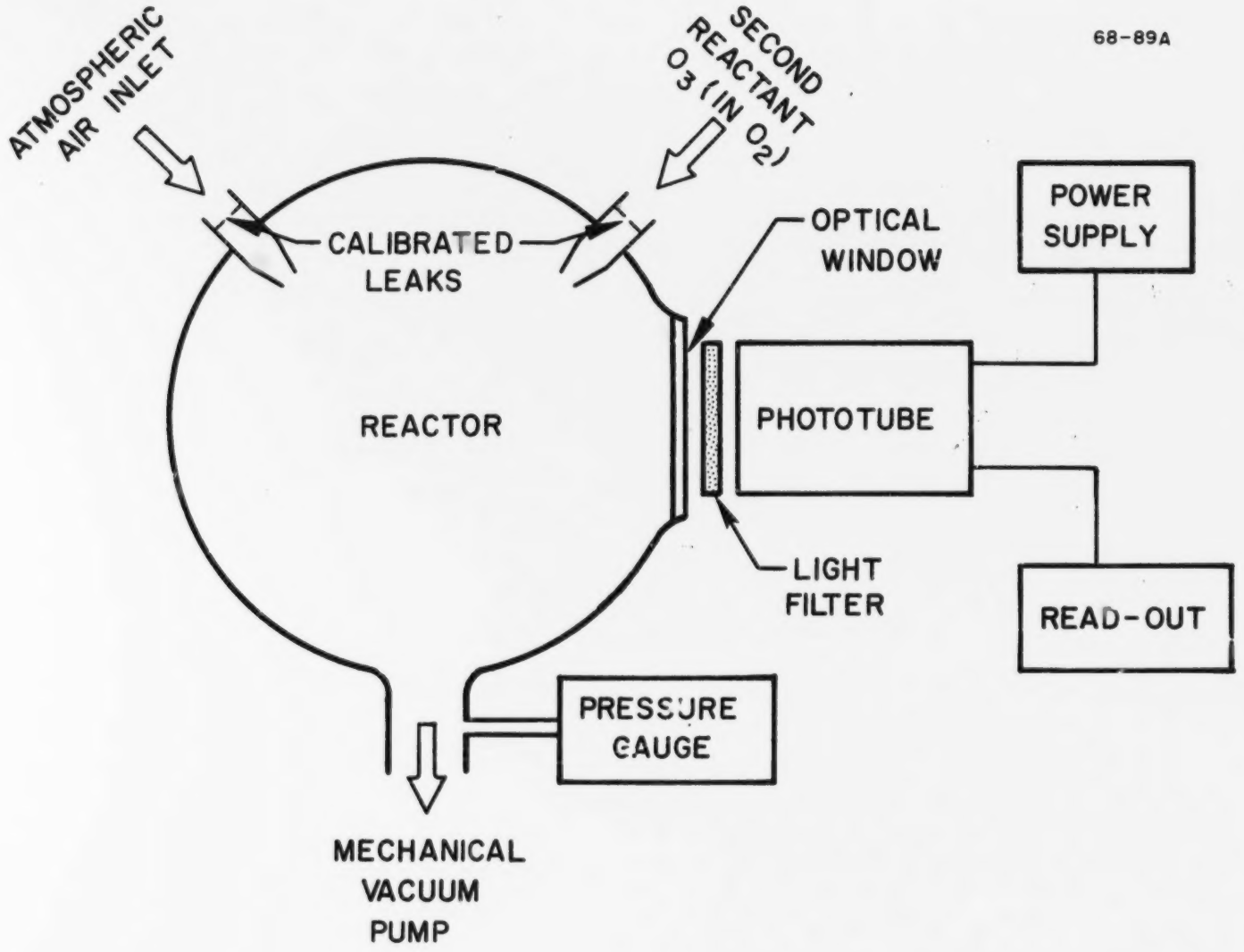


FIG. 1 SCHEMATIC OF THE CHEMILUMINESCENCE NO DETECTOR

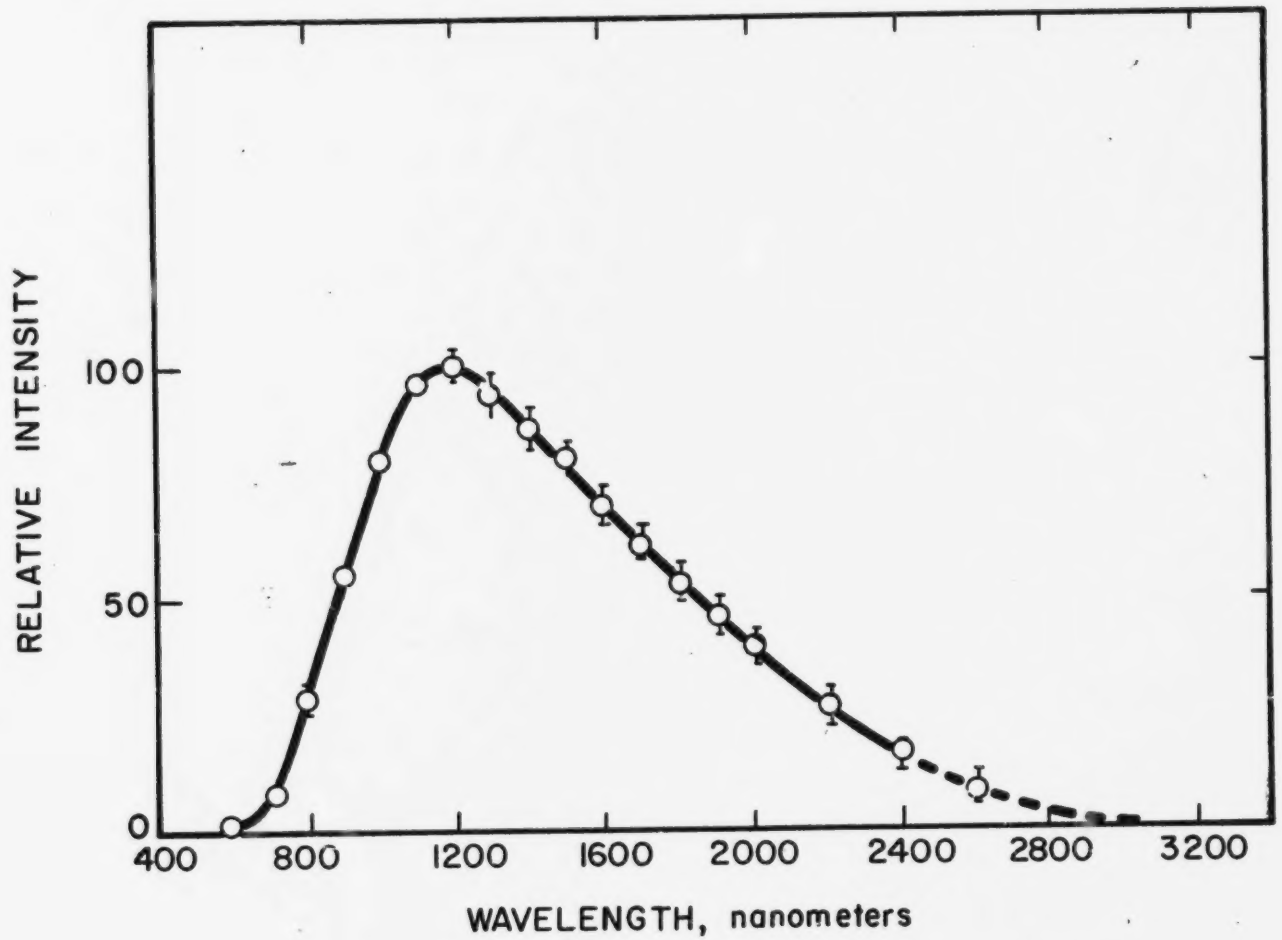


FIG. 2 SPECTRAL DISTRIBUTION OF NO/O_3 EMISSION

Units proportional to quanta per wavelength interval per second.
Spectral distribution normalized to Intensity = 100 at $\lambda = 1.2\ \mu$.
Data after Clough and Thrush, Ref. 4.

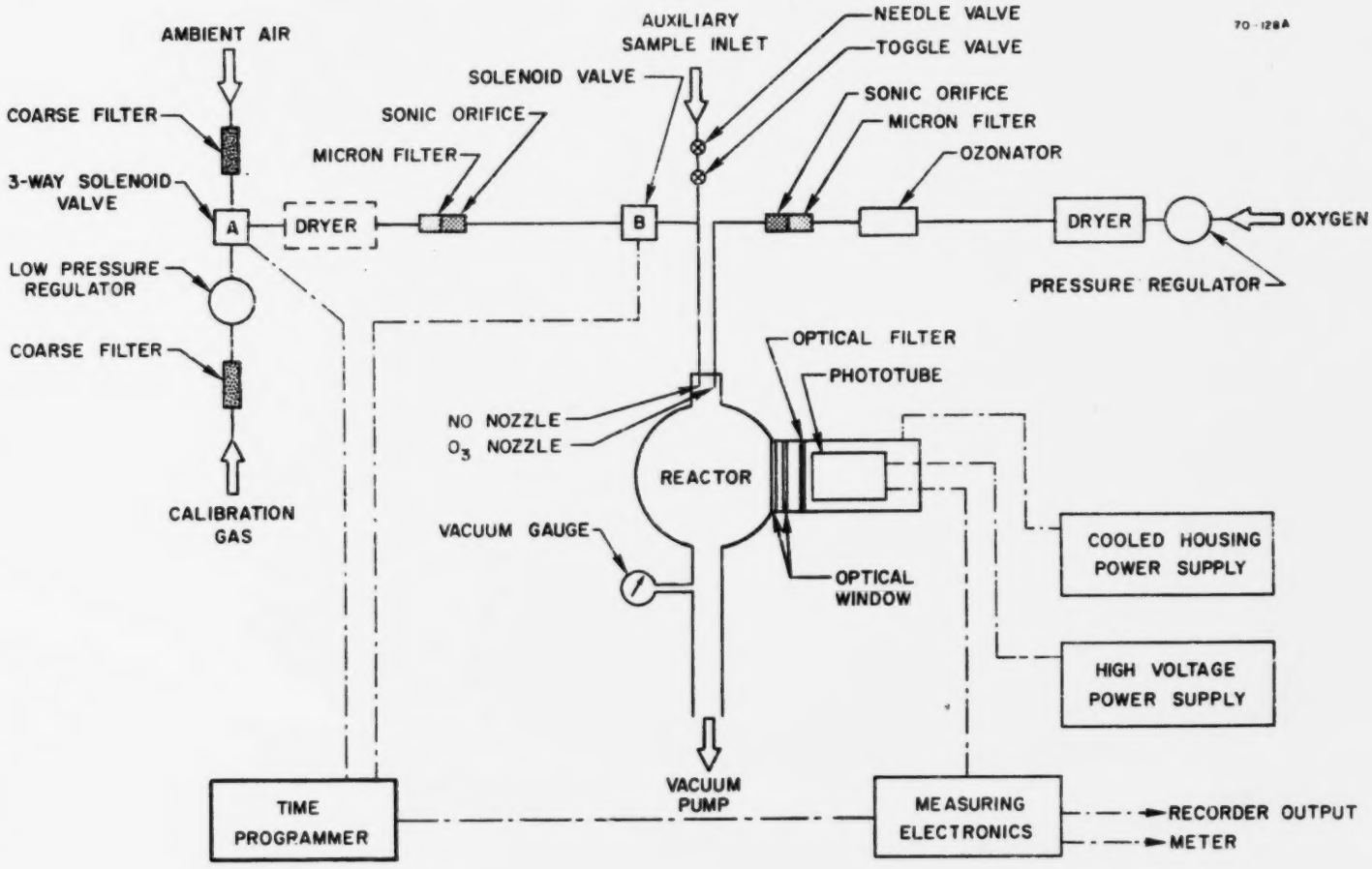


FIG. 3 BLOCK DIAGRAM OF PROTOTYPE NO ANALYZER

FIG. 4 FRONT VIEW OF MONITOR

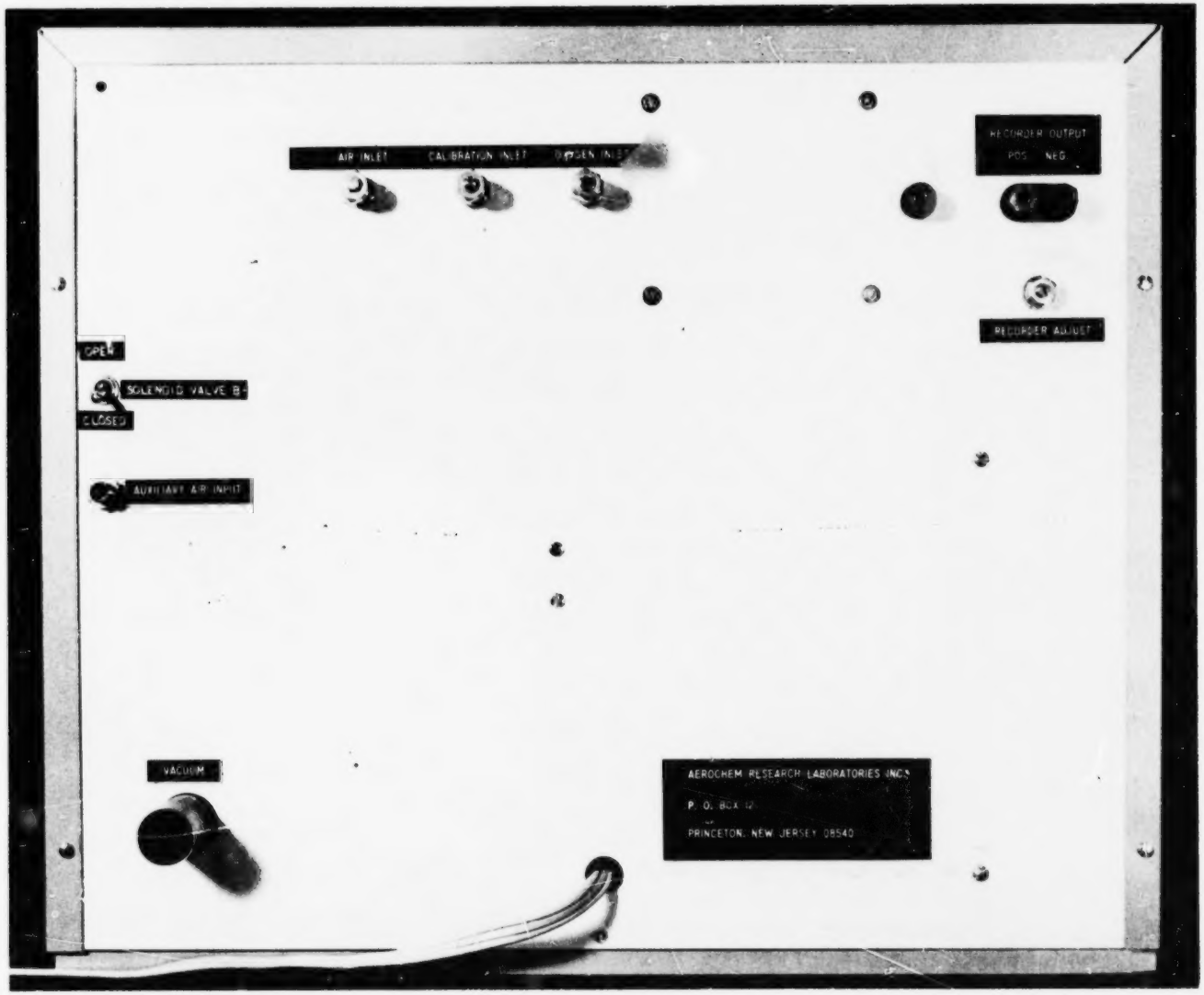


FIG. 5 REAR VIEW OF MONITOR

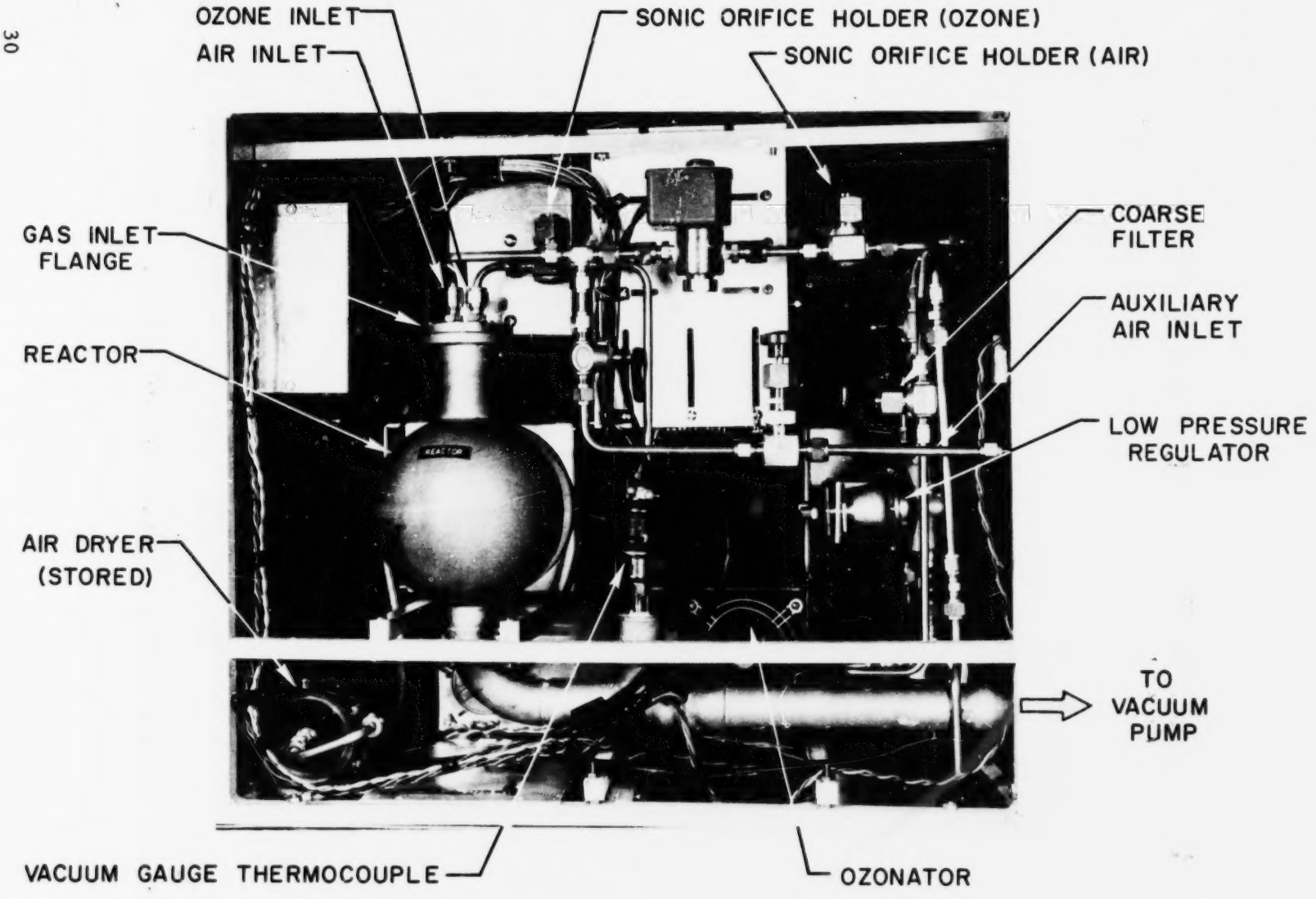


FIG. 6 RIGHT INSIDE VIEW OF MONITOR

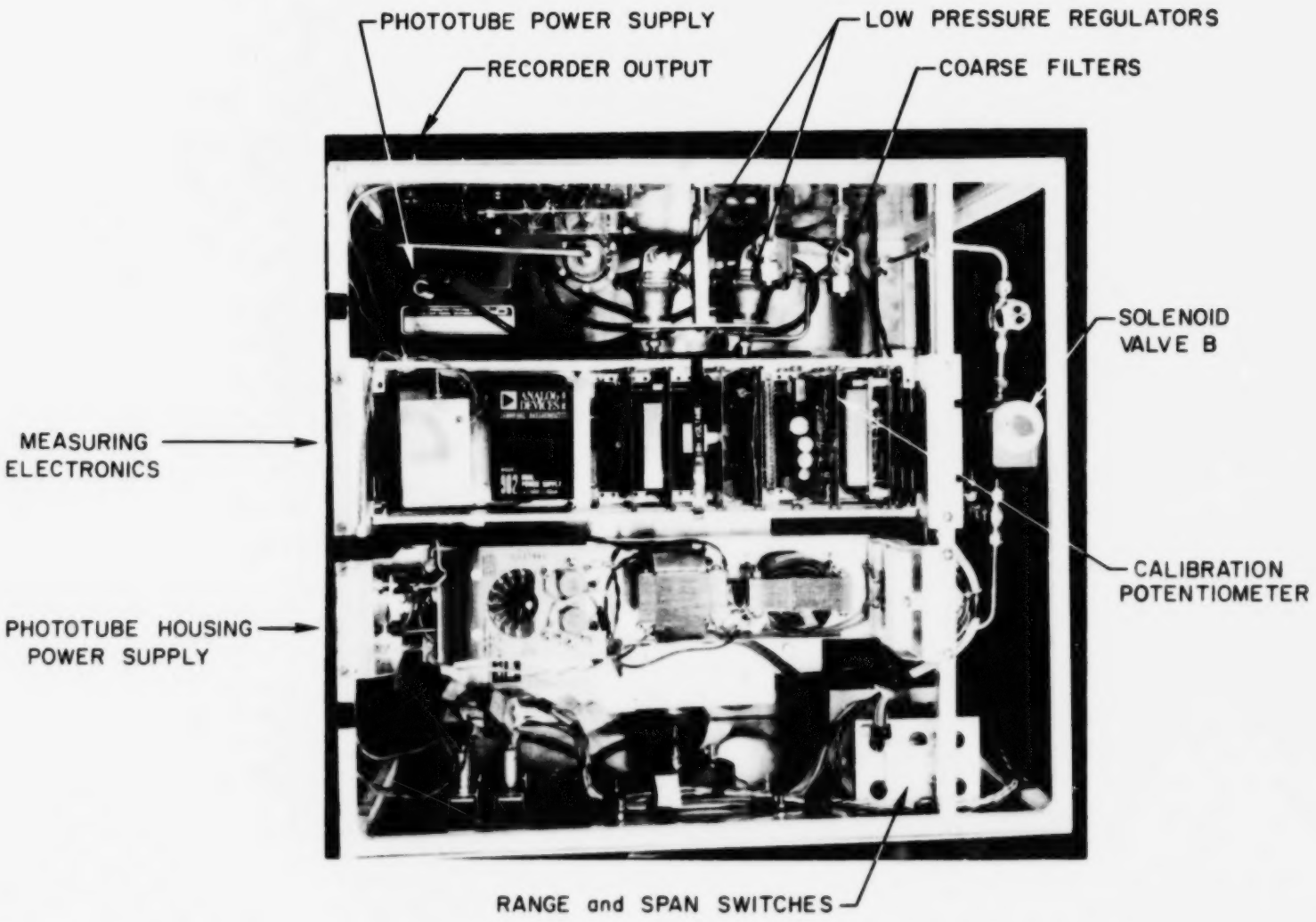


FIG. 7 TOP INSIDE VIEW OF MONITOR

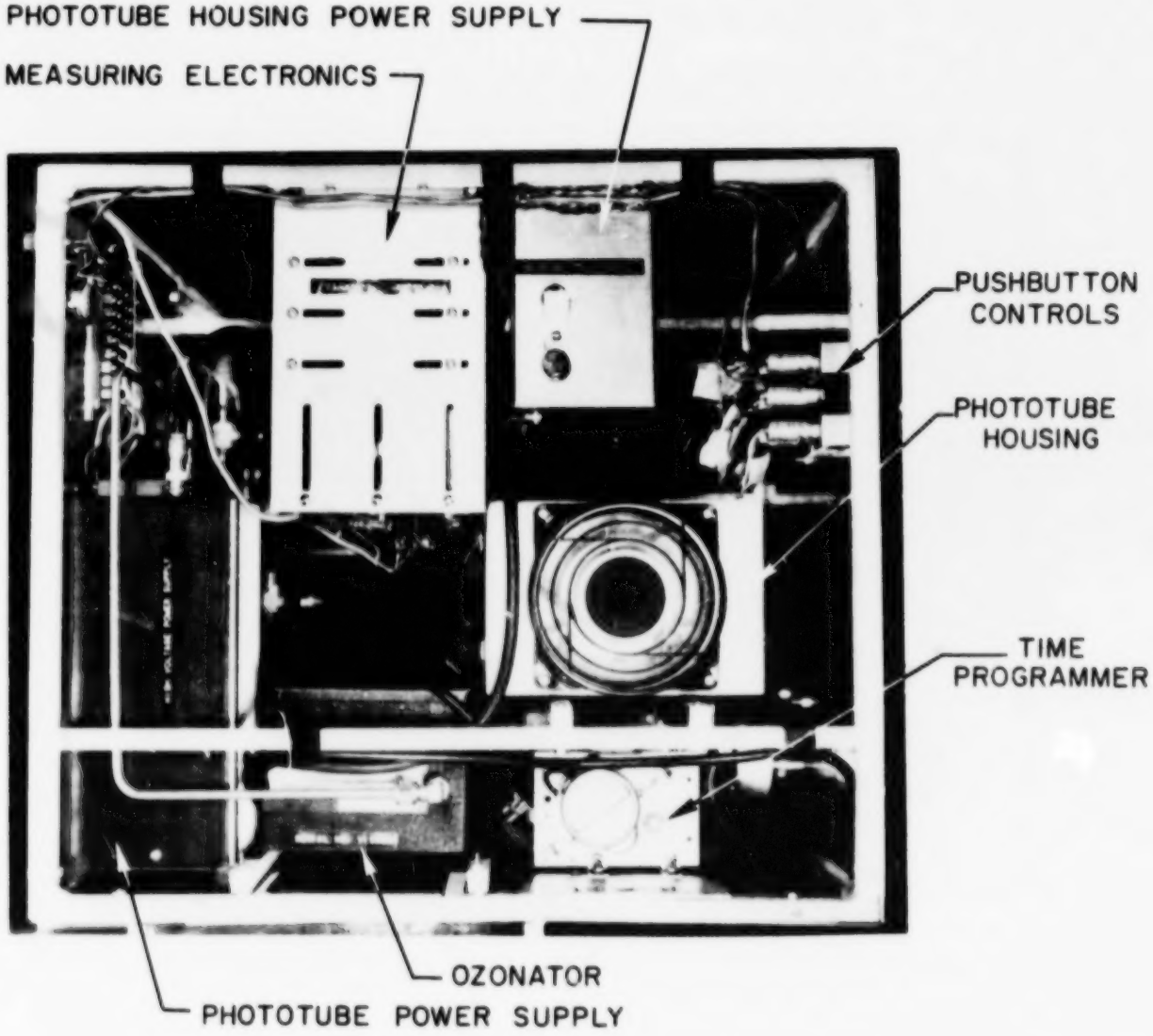


FIG. 8 LEFT INSIDE VIEW OF MONITOR

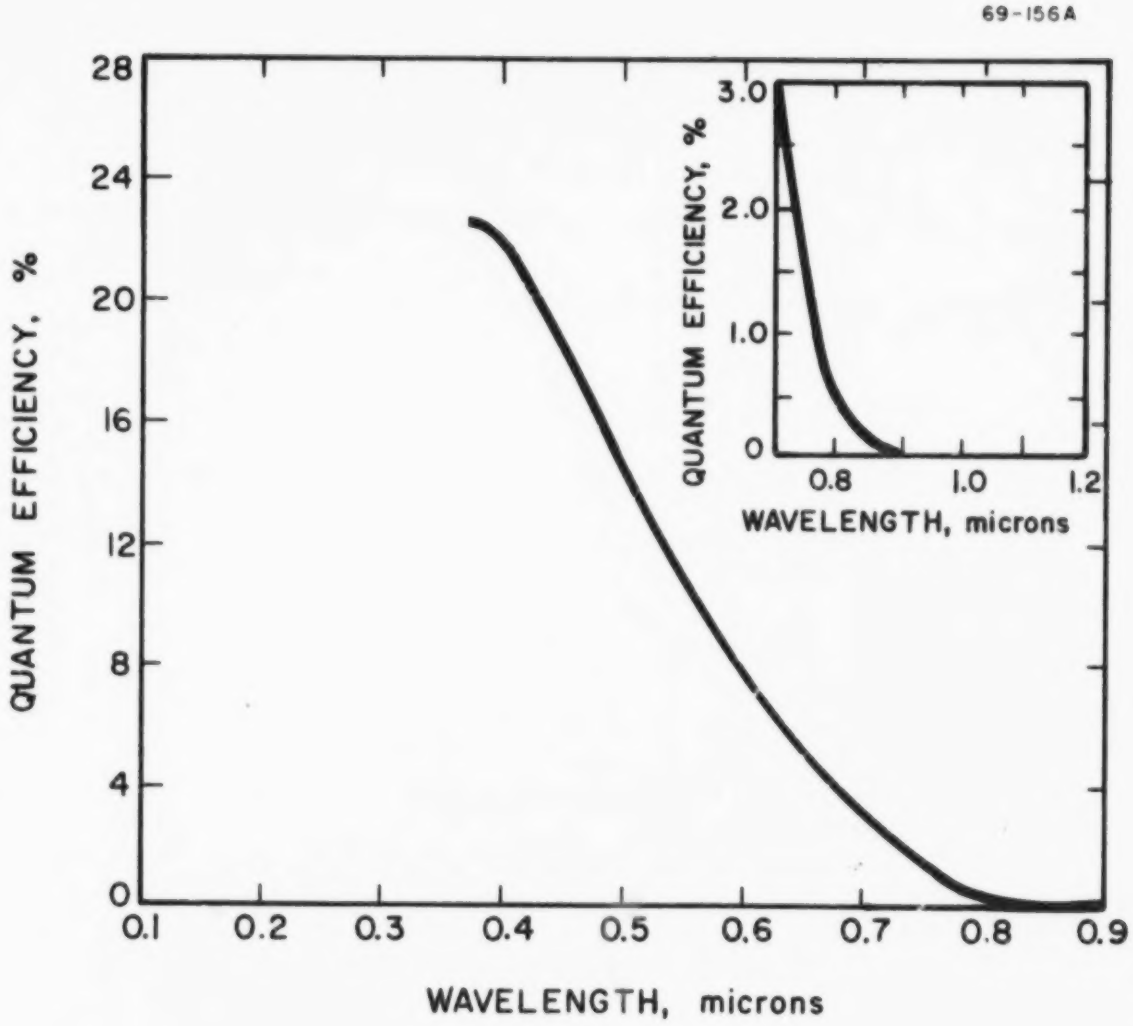


FIG. 9 SPECTRAL RESPONSE OF EMI 9558 A PHOTOMULTIPLIER TUBE

Data from EMI Catalog

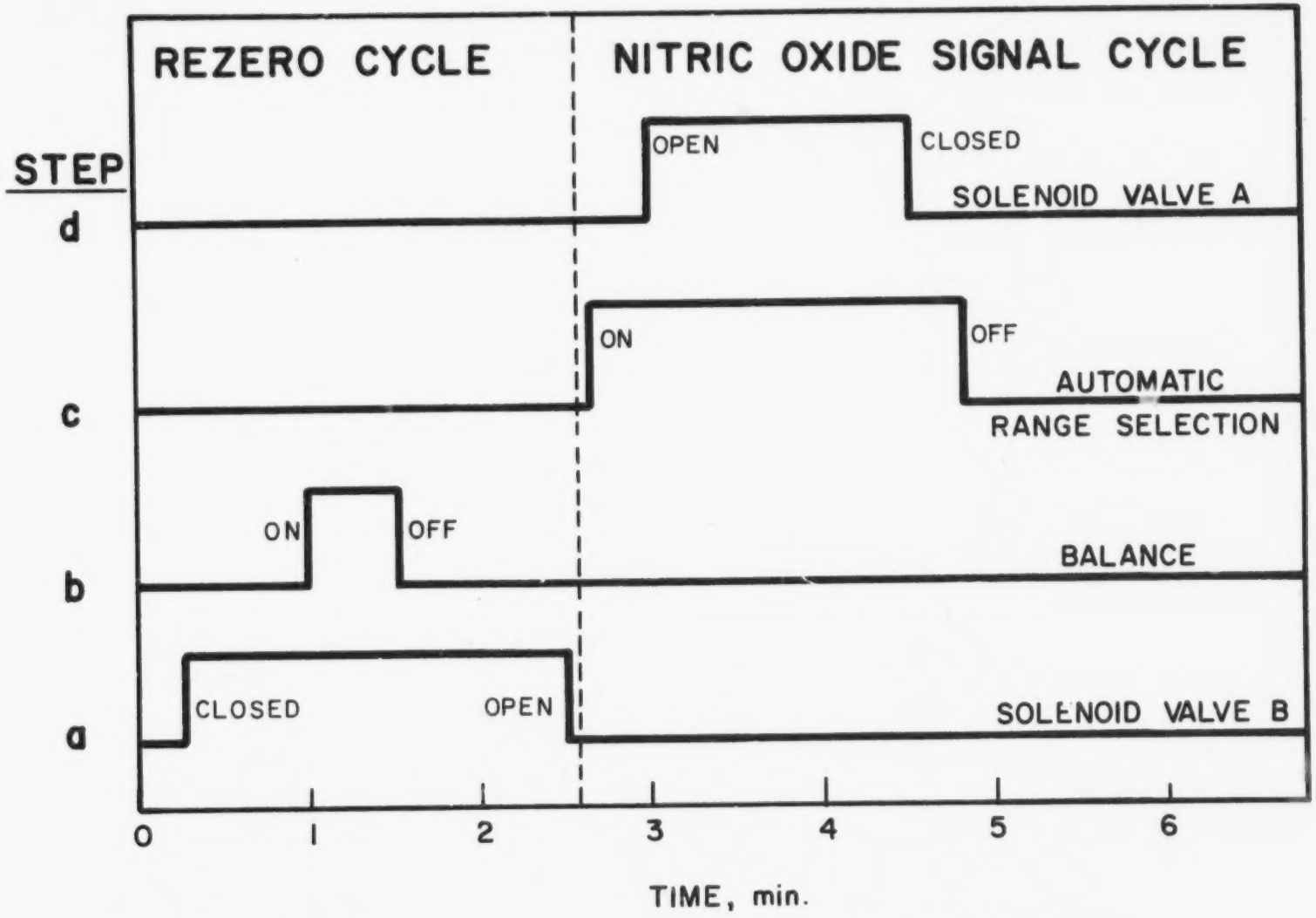


FIG. 10 AUTOMATIC REZERO AND SIGNAL CALIBRATION SEQUENCE

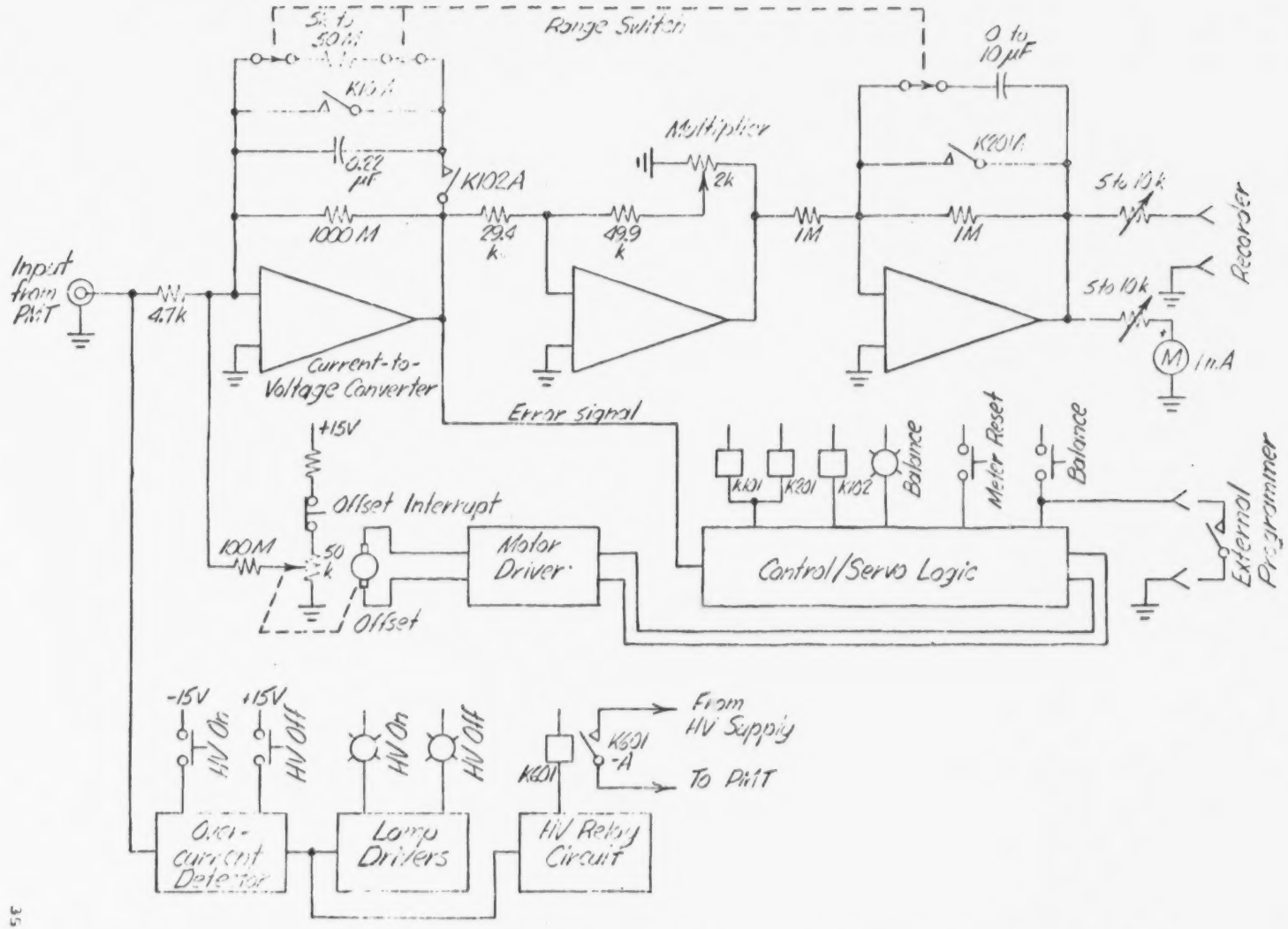


FIG. 11 BLOCK DIAGRAM OF MEASURING ELECTRONICS PACKAGE

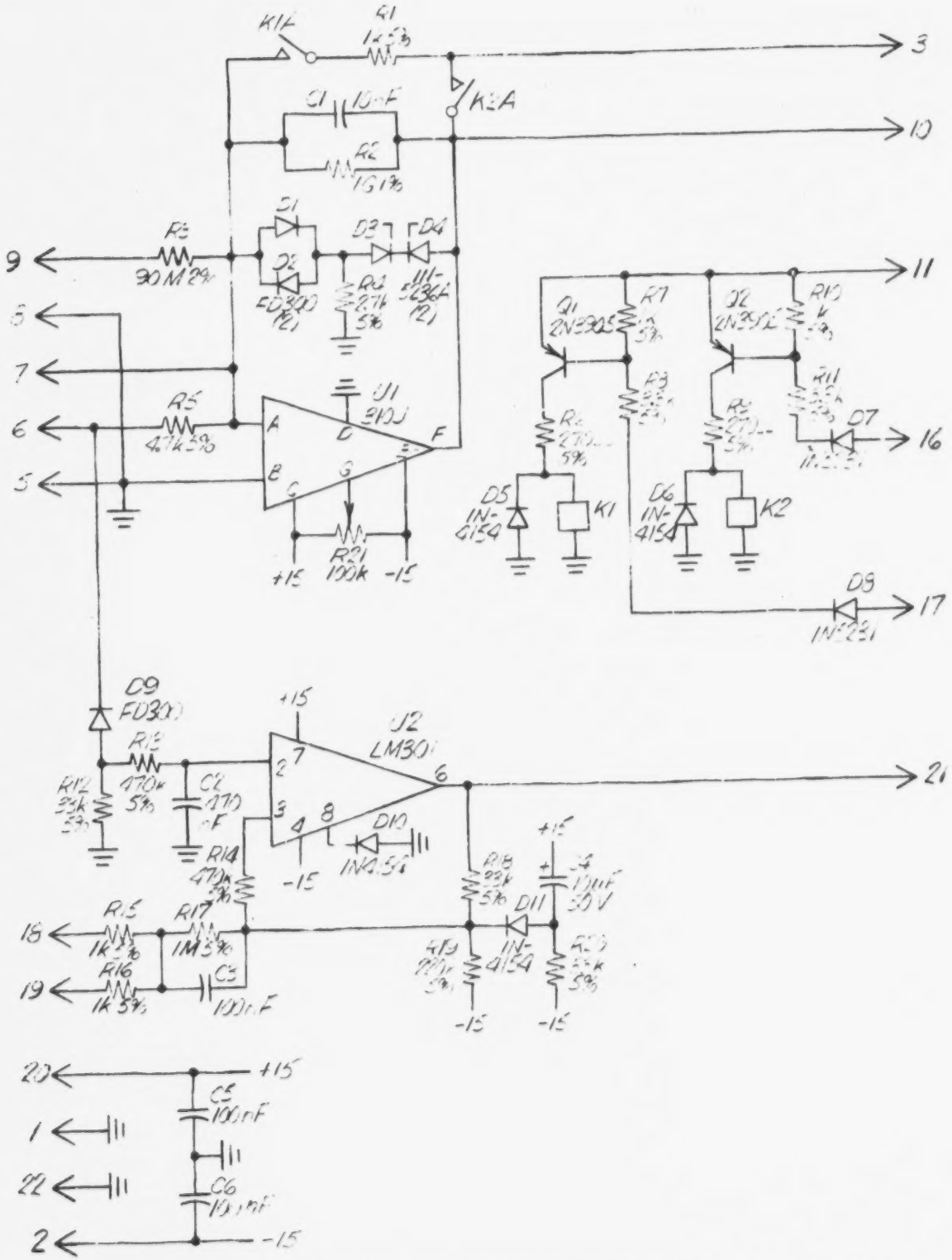
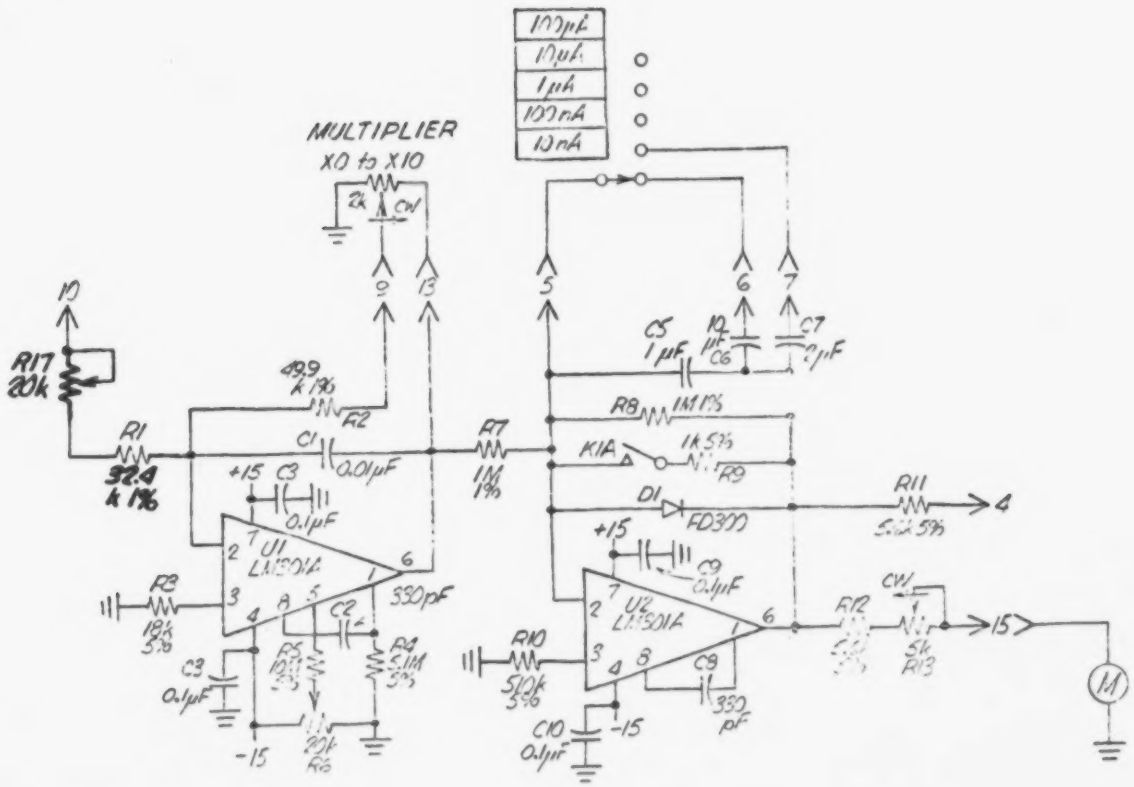


FIG. 12A CURRENT-TO-VOLTAGE CONVERTER CIRCUIT



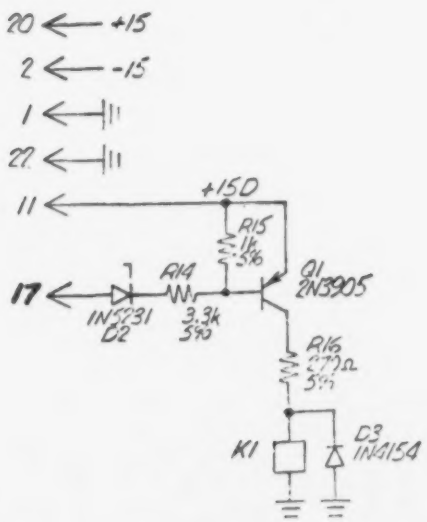


FIG. 12B DC AMPLIFIER/FILTER CIRCUIT

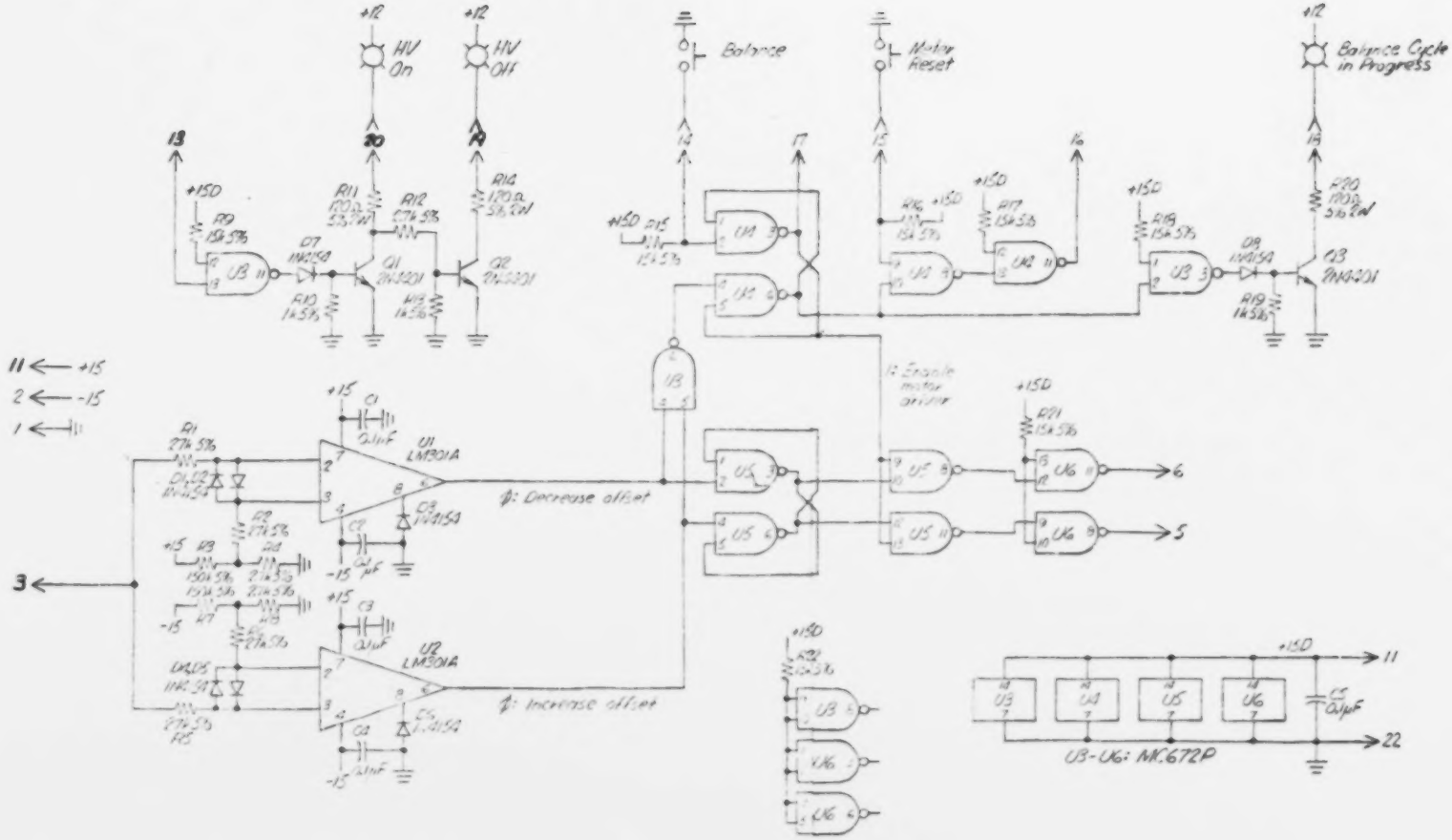
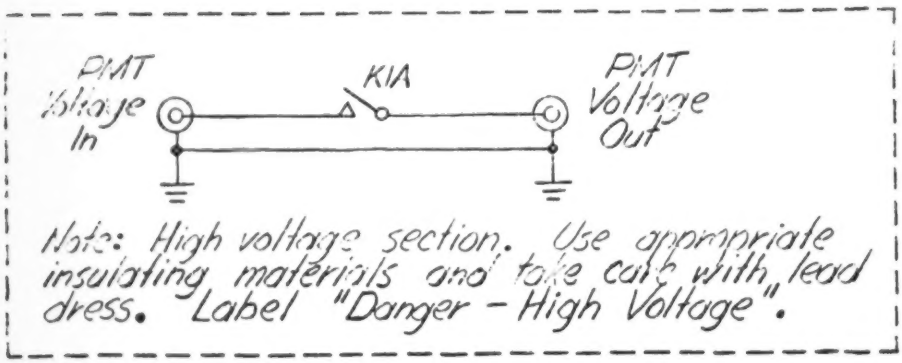


FIG. 12C CONTROL/SERVO LOGIC CIRCUIT



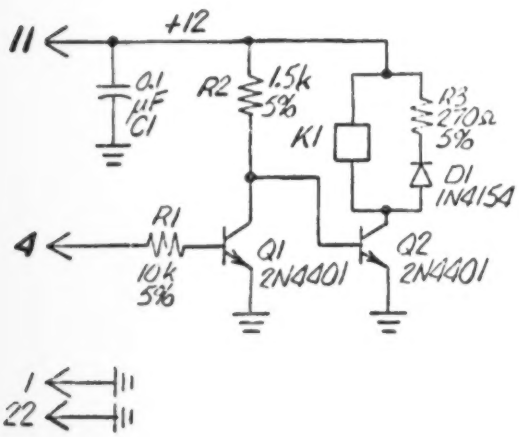
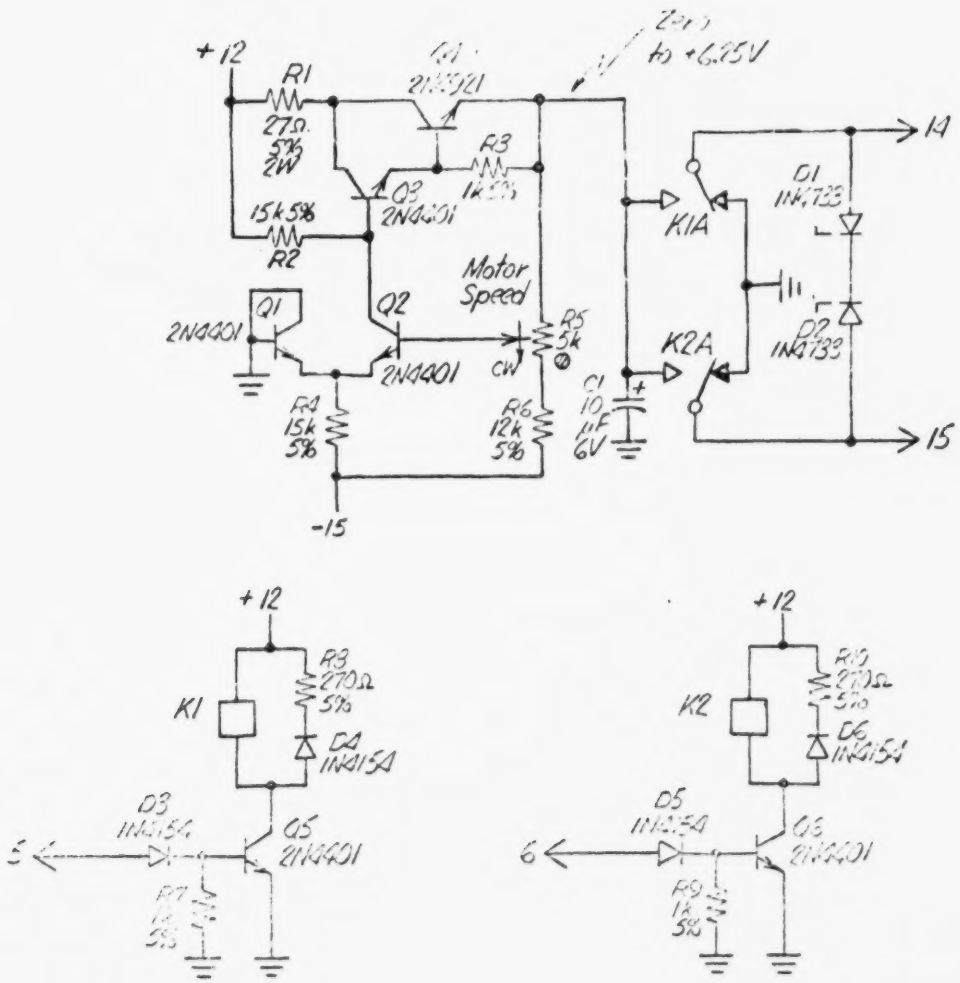


FIG. 12D HIGH VOLTAGE RELAY CIRCUIT



1 ⟵

2 ⟵ -15

20 ⟵ +12

22 ⟵

FIG. 12E MOTOR DRIVER CIRCUIT